MECHANISM OF THE CONVERSION OF N-ALKYLATED AMIDES TO HALOALKANES BY PHOSPHORUS PENTAHALIDES

BY

ERWIN WARD NOMMENSEN

B.S., University of Illinois, 1943
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

Prior to 1875, it was known that the action of phosphorus pentoxide on unsubstituted amides yielded nitriles by dehydration. It was thought that N-alkyl amides would also yield nitriles if a more efficacious dehydrating agent were used (1). Wallach (2), undertaking to find such a reagent, obtained nitriles from N-alkyl amides by the action of phosphorus pentachloride, but found that the reaction was not one of dehydration and that chlorine-containing intermediates and complex by-products were obtained from amides of aliphatic acids. von Pechmann (3) found that N-alkyl amides of aromatic acids, when treated with phosphorus pentahalide, yielded the corresponding aromatic nitrile, alkyl halide, and phosphorus oxyhalide with few complicating side reactions. von Braun (4) pointed out the possibility of employing amides of heterocyclic secondary amines and postulated ring cleavage to yield nitrile and alkylene dihalide. His postulate was confirmed (5) and the reaction has since borne his name. Various types of intermediates have been postulated by previous workers, but the examination of the evidence for the existence of such intermediates also indicates the uncertainty of these representations.

It was considered that greater insight into the probable reaction intermediates could be gained by an examination of the steric nature of the displacement of the C_6H_5CONR-group by halogen and of the fate of asymmetry at the *alpha*-N carbon.

Discussion Of Results

A series of N-alkyl-substituted benzamides was subjected to the von Braun reaction. N-benzoyl-*n*- and *sec*-butylamine

gave good yields of *n*- and *sec*-butyl bromide, respectively. N-benzoyl-*t*-butylamine gave only a trace of *t*-butyl bromide, and N-benzoylneopentylamine gave no neopentyl bromide. These results indicate either that the reaction with the latter two benzamides follows a different course from that of the first two benzamides, or that the halides which may be produced are unstable in the reaction medium. The former alternative is preferred, since *t*-butyl bromide and *t*-amyl bromide (probable rearrangement product of neopentyl bromide) are only partially converted to olefin and hydrogen bromide under simulated von Braun reaction conditions.

This potential generalization of decreasing yields of halide with increasing steric hinderance at the *alpha*-N carbon also held for the N,N-alkylene-substituted benzamide series. von Braun (5) obtained a 78% yield of 1,5-dibromopentane from N-benzoylpiperidine. N-benzoyl-2,6-dimethylpiperidine gave a 19% yield of 2,6-dibromoheptane, and N-benzoyl-2,2,6,6-tetramethylpiperidine gave no dibromide.

Since diminution of yield of halide with increasing steric hinderance to approach the *alpha*-N carbon would be the behaviour expected of a bimolecular nucleophilic substitution reaction, it was desirable to learn whether inversion of configuration occurred at the asymmetric *alpha*-N carbon. Optically pure N-benzoyl-*d*-*sec*-butylamine was converted to *l*-*sec*-butyl bromide in 60% yield by the action of phosphorus pentabromide (*d* and *l* refer only to directions of rotation). This inversion of sign of rotation corresponds to an inversion of configuration (6) to an extent which is in the range of that observed in other reactions commonly considered to bring about inversion (7).

Hindrance to approach at the carbon of the carbonyl group was found not to inhibit the reaction: N-mesitoyl-*n* and *sec*-butylamine gave satisfactory yields of alkyl halide.

A mechanism for the von Braun reaction has been suggestd which is consistent with the previous findings on the reaction and with the new observations discussed above.

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VITA

The author was born in Denver, Colorado, on November 23, 1921, and attended the public schools of that city. He was graduated from high school and junior college in Joplin, Missouri. In 1943, he obtained the degree of Bachelor of Science from the University of Illinois and entered the U. S. Naval Reserve. He was trained as a meteorologist and chemical warfare officer, and served as such in the Southwest Pacific theater. He was released to inactive duty in 1946, and returned to the University of Illinois where, in 1947, he obtained the degree of Master of Science. During the course of his graduate work, he has held teaching assistantships in the departments of mathmatics and chemistry.

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